PATENT SPECIFICATION (11) 1296511

NO DRAWINGS

(21) Application No. 383/70 (22) Filed 5 Jan. 1970

(31) Convention Application No. 789374 (32) Filed 6 Jan. 1969 in

(33) United States of America (US)

(45) Complete Specification published 15 Nov. 1972

(51) International Classification D21H 3/08

(52) Index at acceptance D2B 11B 14A 14E 14H 14X

(54) SURFACE TREATMENT OF PRE-FORMED FIBROUS CELLULOSIC SUBSTRATES

PATENTS ACT 1949

SPECIFICATION NO 1296511

The following amendments were allowed under Section 29 on 12 July 1974

Page 1, line 29, *after* of *insert* certain

Page 1, line 33, page 5, lines 15, 57 and 61 *after* web *insert* that is a paper web, sheet or board,

Page 1, *delete* lines 48, 49 and 50

Page 1, line 74, *delete* paper

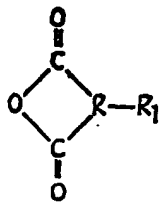
THE PATENT OFFICE
8 August 1974

R 77126/7

agent is applied to the surface of an already formed substrate. This invention is particularly concerned with the surface treatment procedure.

It is an object of the present invention to provide an efficient, economical method for surface sizing of fibrous cellulosic substrates and more particularly of paper.

According to the present invention there is provided a method of sizing a pre-formed cellulosic-fibre-containing web which method comprises applying to the surface of the preformed web a sizing amount of a cyclic dicarboxylic acid anhydride of the formula



twelve or more carbon atoms provide the optimum results in surface sizing of fibrous substrates. Mixtures of the anhydrides may be employed in the practice of the invention.

The anhydrides are preferably applied in the form of aqueous dispersions.

If it is found desirable, surfactants may be used as emulsifying agents for the sizing agents in the practice of this invention. Surfactants which may be used include polyoxyethylene-sorbitan trioleate, polyoxyethylene - sorbitol hexaoleate, polyoxyethylene - sorbitol laurate and polyoxyethylene - sorbitol oleate - laurate.

Cellulosic paper webs which may be sized in accordance with this invention include both paper and fiber-boards obtained from conventionally prepared pulps, e.g. sulfite, sulfate, rag-stock pulps and papers containing pigment fillers such as clay or titanium dioxide and products derived from combinations of cellulosic pulps and various man-made pulps and fibers such as polyacrylonitrile, polyamide, polyester fibers and regenerated cellulose. The paper treated in accordance with this inven-

SPECIFICATION AMENDED - SEE ATTACHED SLIP

PATENT SPECIFICATION

(11) 1296511

1296511

NO DRAWINGS

(21) Application No. 383/70 (22) Filed 5 Jan. 1970

(31) Convention Application No. 789374 (32) Filed 6 Jan. 1969 in

(33) United States of America (US)

(45) Complete Specification published 15 Nov. 1972

(51) International Classification D21H 3/08

(52) Index at acceptance D2B 11B 14A 14E 14H 14X

(54) SURFACE TREATMENT OF PRE-FORMED FIBROUS CELLULOSIC SUBSTRATES

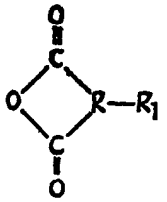
(71) We, MONSANTO COMPANY, a corporation organised under the laws of the State of Delaware, United States of America, of 800, North Lindbergh Boulevard, St. Louis 66, State of Missouri, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the surface treatment of pre-formed fibrous cellulosic substrates.

Current procedures for treatment of cellulosic fibrous substrates such as paper involve two principle methods of application. One method concerns internal treatment wherein the treating agent is mixed with the fiber furnish and thereafter the entire mass is formed into a sheet having a uniform distribution of fibers and treating agent. Another method involves surface treatment wherein the treating agent is applied to the surface of an already formed substrate. This invention is particularly concerned with the surface treatment procedure.

It is an object of the present invention to provide an efficient, economical method for surface sizing of fibrous cellulosic substrates and more particularly of paper.

According to the present invention there is provided a method of sizing a pre-formed cellulosic-fibre-containing web which method comprises applying to the surface of the preformed web a sizing amount of a cyclic dicarboxylic acid anhydride of the formula



wherein R represents a dimethylene or trimethylene group and R_1 represents a group containing more than 5 carbon atoms and being an alkyl, alkenyl, aralkyl or aralkenyl group.

In a modification of this method, there is employed a cyclic dicarboxylic acid anhydride of the above formula in which R is is defined above and R_1 represents an aralkoxy or alkoxy group containing more than 5 carbon atoms.

The cellulosic web is preferably a paper web, sheet or board, or a mat of cellulose-containing fibers pressed to any desired shape.

Examples of the above described anhydrides are *iso*octadecenyl - succinic acid anhydride, *n* - hexadecenyl - succinic acid anhydride, dodecyl - succinic acid anhydride, decenyl - succinic acid anhydride, octenyl - succinic acid anhydride, nonenyl - succinic acid anhydride, triisobutenyl - succinic acid anhydride, caprylyoxy - succinic anhydride, heptyl - glutaric acid anhydride and benzyloxy - succinic acid anhydride. Acid anhydrides in which R_1 contains twelve or more carbon atoms provide the optimum results in surface sizing of fibrous substrates. Mixtures of the anhydrides may be employed in the practice of the invention.

The anhydrides are preferably applied in the form of aqueous dispersions.

If it is found desirable, surfactants may be used as emulsifying agents for the sizing agents in the practice of this invention. Surfactants which may be used include polyoxyethylene-sorbitan trioleate, polyoxyethylene - sorbitol hexaoleate, polyoxyethylene - sorbitol laurate and polyoxyethylene - sorbitol oleate - laurate.

Cellulosic paper webs which may be sized in accordance with this invention include both paper and fiber-boards obtained from conventionally prepared pulps, e.g. sulfite, sulfate, rag-stock pulps and papers containing pigment fillers such as clay or titanium dioxide and products derived from combinations of cellulosic pulps and various man-made pulps and fibers such as polyacrylonitrile, polyamide, polyester fibers and regenerated cellulose. The paper treated in accordance with this inven-

tion may be waterleaf, slacksized or hard-sized paper.

The cyclic dicarboxylic acid anhydride derivative may be used as the sole sizing agent in amounts sufficient to impart the required sizing properties. However, it is particularly preferred to mix the cyclic dicarboxylic acid anhydride with starch, a starch derivative or a proteinaceous material.

The cyclic dicarboxylic acid anhydride derivative may be mixed *per se*, or in aqueous dispersed form, with starch, starch derivative, or proteinaceous material such as casein, or soybean protein to improve the properties of the starch or protein sizing applied to the cellulosic substrate. Although any desired proportions may be used, it is generally contemplated to mix from 1 percent to 95% of the sizing agent with the starch or protein, based on the weight of the starch or protein to which it is added. It is particularly preferred to use from 1% to 8% of the sizing agent based on the weight of the starch or protein to which it is added. While the sizing agent may be mixed with starch prior to cooking, it is preferred to add the sizing agent after the starch is cooked and as near to the time of application as possible.

The starches and starch products with which these sizing agents may be mixed are those which are commonly used in cellulosic-web surface-sizing and coating applications including corn starch, potato starch, sago starch, wheat starch, and also the various starch products and derivatives including British gums, enzyme-converted starches, hydroxyethylated starches, oxidized starches and cationic starches having quaternary ammonium or other amine salt groups therein. A typical cationic starch is a modified corn starch having a nitrogen content of about 0.25 percent sold under the tradename "Cato 8" by National Starch Products Company.

The sizing solution can be applied to paper by running either dry or wet paper from the paper-making machine through the sizing solution. Alternatively, the sizing solution can be applied to the paper by spraying the paper with the sizing solution at any stage in its manufacture or by roll-coating the paper. Any other method of applying a sizing solution to paper known *per se* in the paper making art may alternatively be employed.

The following examples illustrate the advantageous and unexpected properties which are achieved by the use of the sizing agents of the present invention for the surface sizing of the fibrous substrates. Unless otherwise stated, all percentages cited in the examples below are based on weight.

The test methods used to determine the physical properties of the paper treated with the sizing agent of this invention are listed below with the explanatory notes where necessary. Samples were conditioned according to TAPPI T402m-49 before testing. The paper base stock used in the testing hereinafter described is 50 lb. bleached Kraft.

Ink Penetration—A permanent Blue-Black ink is acidified to a pH of 1.5 by the addition of concentrated hydrochloric acid. A sample of the ink is poured into a tray and held at a temperature of 33°C. The paper sample to be tested is placed on the ink, wire side down. The time in seconds is recorded from the moment of contact of the paper with the ink until the reflectance of the paper has dropped to a visually estimated 85% of its initial value due to the penetration of the ink. The time, in seconds, is the reported test value.

Surface Energy Test—A set of standard mixtures of ethyl alcohol and water having a range of surface tensions of from 72 dynes per cm (pure water) to about 30 dynes per cm (approximately 40% alcohol) in water are used to determine the surface energy characteristics of the treated paper. The paper to be tested is placed against a dark background. Drops of the standard mixtures of alcohol and water are placed on the paper until a liquid is found which quickly produces a saturated spot on the sheet. Another standard liquid is then found by the same procedure which will not produce a saturated spot for at least 20 seconds. Since the liquids of lower surface tension (more alcohol) are more penetrating, the drop which saturates will come from a lower-tension mixture. The gap between the two initial test drops is narrowed to determine a liquid which saturates in less than 20 seconds. The paper has a surface energy equal to the surface tension of the liquid which saturated the sheet in less than 20 seconds.

Fold Endurance—The fold endurance is determined according to a test known as the "MIT Folding Endurance" test and is described under TAPPI designation T-423m-50. Folding endurance is a measure of the strength of the treated paper and is recorded as the total number of double folds required to sever the paper at the crease when a uniform folding rate (175 double folds per minute) is used and the strip is under a tension of 1.5 kg.

Dry Tensile Test—Dry tensile tests are run on 0.5 x 7 inch strips of paper according to a test described under TAPPI designation T404-05-61.

Bursting Strength Test—The bursting strength of paper is run on a Mullen Bursting Tester according to a test described under TAPPI designation T-403ts-63.

Examples 1—7

Handsheets having a Gurley porosity of 16 seconds are prepared from a 50% softwood/50% hardwood kraft pulp having a Canadian Standard Freeness of 280. The resulting handsheets are dried for 2 minutes at 209°F. The

sheets are then surface-sized in a size press, conditioned at 73°F and 50 percent relative humidity and tested for sizing efficiency as tabulated in Table I.

TABLE I

Example No.	% Conc. of Additives at Size Press		Pounds Sizing Agent Per Ton Paper	Ink Penetration Sec[5]	Surface Energy Dynes/cm[5]	Dry Tensile lbs/in[6]	Folds to Break[6]	(Mullen lbs/in²)[6]
	Starch[1,2]	Sizing Agent[3,4]						
1	—	—	—	0	72	20	44	34
2	3.0[7]	—	—	0	72	28	234	68
3	3.0[7]	1.25	1.0	8	60	29	330	59
4	3.0[7]	2.5	2.0	1029	34	28	260	58
5	3.0[7]	6.25	5.0	820	33	23	137	57
6	3.0[7]	12.5	10.0	244	35	23	100	48
7	3.0[7]	25.0	20.0	26	36	24	75	51

[1]Penford Gum — P—280 — hydroxyethylated starch
[2]Percent in size press solution
[3]Percent based on wt. of starch
[4]*n*-Hexadecenyl-succinic acid anhydride
[5]Cure — 1 hour
[6]Cure — 24 hours
[7]75—80 lbs starch/ton paper

Results similar to those obtained with Examples 3 to 7 of Table I are obtained when the following substituted cyclic dicarboxylic acid anhydrides are used in place of the *n*-hexadecenyl succinic acid anhyride:

(1) dodecenyl - succinic acid anhydride
(2) dodecyl - succinic acid anhydride
(3) *iso* - octadecenyl - succinic acid anhydride
(4) mixture of iso - alkenyl - succinic acid anhydrides wherein the alkenyl groups contain from 18 to 22 carbon atoms.

Examples 8—13 (Comparison)

By way of contrast, handsheets are prepared in a manner identical to the procedure of Examples 1 to 7 with the exception that the pulp slurry is treated with varying amounts of the sizing agent and cationic starch shown in Table II. The sizing efficiency of these internally sized papers of these examples are shown in Table II.

TABLE II

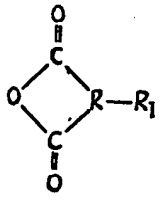
Example No.	% Conc. of Additives to Pulp[1]		Pounds Sizing Agent Per Ton Paper	% Conc. Starch[4] at Size Press	Ink Penetration Sec[5]	Surface Energy Dynes/cm[5]	Dry Tensile lbs/in[6]	Folds to Break[6]	[Mullen lbs/in²][6]
	Sizing Agent[2]	Cationic Starch[3]							
8	0.1	0.1	2.0	4.0[7]	3	50	28	190	62
9	0.25	0.25	5.0	4.0[7]	46	44	26	135	60
10	0.25	0.25	5.0	—	90	50	20	28	31
11	0.5	0.5	10.0	4.0[7]	689	36	25	40	48
12	0.5	0.5	10.0	—	145	43	18	23	30
13	1.0	1.0	20.0	4.5[7]	952	36	21	25	41

[1]Based on wt. of dry pulp
[2]*n*-Hexadecenyl-succinic acid anhydride
[3]"Cato 8" — Modified corn starch having a nitrogen content of about 0.25 percent sold by National Starch Products Company
[4]Penford Gum — P—280 — hydroxyethylated starch
[5]Cure — 1 hour
[6]Cure — 24 hours
[7]75—80 lbs starch/tom paper

From the foregoing results in Table I and II, it is readily apparent that the fibrous substrates which are surface sized as shown in Table I exhibit outstanding, superior and improved performance characteristics over fibrous substrates which have been internally sized as shown in Table II. Additionally, it should be noted that the outstanding properties exhibited in Table I are obtained without the use of a retention aid or a cationic agent, such as a cationic starch, which is deemed necessary for the internally sized substrates.

WHAT WE CLAIM IS:—

1. A method of sizing a pre-formed cellulosic-fibre-containing web, which method comprises applying to the surface of the pre-formed web a sizing amount of a cyclic dicarboxylic acid anhydride of the formula



wherein R represents a dimethylene or trimethylene group and R_1 represents a group containing more than 5 carbon atoms and being an alkyl, alkenyl, aralkyl, or aralkenyl group.

2. A modification of the method of Claim 1 wherein there is employed a cyclic dicarboxylic acid anhydride wherein R in the formula represents a dimethylene or trimethylene group and R_1 represents an aralkoxy or alkoxy group containing more than 5 carbon atoms.

3. A method according to Claim 1 wherein the pre-formed web is a paper web.

4. A method according to either of Claims 1 and 3 wherein the cyclic dicarboxylic acid anhydride is applied to the surface of the web in association with a starch or protein.

5. A method according to Claim 4 wherein the anhydride is applied in association with a hydroxyethylated starch.

6. A method according to either of Claims 4 and 5 wherein the amount of the anhydride is from 1 to 8% by weight of the associated starch or protein.

7. A method according to any of Claims 1 and 3 to 6 wherein the anhydride is one in which the group represented by R_1 in the formula contains 12 or more carbon atoms.

8. A method according to Claim 7 wherein the cyclic dicarboxylic acid anhydride is n-hexadecenyl - succinic acid anhydride.

9. A method according to Claim 7 wherein the cyclic dicarboxylic acid anhydride is *iso*-octadecenyl - succinic acid anhydride.

10. A method according to Claim 1 substantially as described with reference to any one of the Examples 3 to 7.

11. A cellulosic-fibre-containing web having at its surface a size, whenever prepared by a method according to any of Claims 1 and 3 to 10.

12. A cellulosic-fibre-containing web having at its surface a size, whenever prepared by a method according to Claim 2.

J. C. LUNT,
Chartered Patent Agent,
Monsanto House, 10—18 Victoria Street,
London, SW1H ONQ.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1972.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.